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Identification of allanite $(Ce,Ca,Y)_2(Al,Fe^{3+})_3(SiO_4)_3OH$ found in marble from Chillagoe, Queensland using Raman spectroscopy

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Abstract:

Samples of marble from Chillagoe, North Queensland have been analysed using scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and Raman spectroscopy. Chemical analyses provide evidence for the presence of minerals other than limestone and calcite in the marble, including silicate minerals. Some of these analyses correspond to silicate minerals. The Raman spectra of these crystals were obtained and the Raman spectrum corresponds to that of allanite from the Arizona State University data base (RRUFF) data base. The combination of SEM with EDS and Raman spectroscopy enables the characterisation of the mineral allanite in the Chillagoe marble.

Keywords: allanite, epidote, silicate, marble, Raman spectroscopy, SEM, EDS

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Introduction

Extensive marble deposits occur in the mining town of Chillagoe, Atherton Tableland, Queensland. Chillagoe is historically famous for the mining of gold, copper and zinc. Extensive limestone caves exist in the Chillagoe-Mungana area. The geology of the Chillagoe region is complex and diverse. The extraction of marble from the Chillagoe deposits is illustrated in Figure1. Extensive variation in the marble is found with an example of the quality marble illustrated in Figure 2. Three types of marble are found including 'soft' marble which is readily cut and 'hard' marble which is difficult to cut and destroys the diamond cutting blades. It is suggested that microdiamonds exist in this type of marble. Black marble is also found. For the soft marble, few distinct crystals are noted whereas in the hard marble different types of crystals are readily observed.

Allanite belongs to the sorosilicate group of minerals within the broader epidote group that contains a significant amount of rare earth elements (REE).The mineral occurs mainly in metamorphosed clay rich sediments and felsic igneous rocks. It has the general formula $A_2M_3Si_3O_{12}[OH]$ where the A sites can contain large cations such as Ca^{2+}, Sr^{2+}, and REE and the M sites admit Al^{3+}, Fe^{3+}, Mn^{3+}, Fe^{2+}, or Mg^{2+} among others. However, a large amount of additional elements, including Th, U, Zr, P, Ba, Cr and others may be present in the mineral. The International Mineralogical Association (IMA) lists three minerals in the allanite group, each recognized as a unique mineral: allanite-(Ce), allanite-(La) and allanite-(Y), depending on the dominant rare earth present, being cerium, lanthanum or yttrium.

There have been some Raman spectroscopic studies of geological materials [1, 2] used as building materials. The study by Jehlicka et al. identified graphitic particles in marbles from Bohemian Massif (Czech Republic) [3]. Raman spectroscopy has been used to study marble statues of archaeological significance [4]. Raman spectroscopy has proven very useful for the study of minerals and their mineral structure, including silicate minerals [5-9]. In this research, we have undertaken a SEM with EDS and Raman spectroscopic study of allanite found in Chillagoe marble.

Experimental

Samples description and preparation

A sample of hard shiny marble was used for the analysis. Crystals were selected for Raman spectroscopic analysis. Please see the graphical abstract for the placement of the allanite.

Raman microprobe spectroscopy

Samples of selected crystals in marble were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The laser beam was focused on individual crystals. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 200 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. Raman spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The Raman spectrum of allanite has been downloaded from the RRUFF data base and is used for a comparison of the allanite crystals found in the marble.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian-Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed at QUT. Marble crystals were coated with a 5nm layer of evaporated carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a

ThermoNORAN spectrometer model Quest and were applied to support the mineral characterization.

Results and discussion

Mineral characterization

The EDS spectra are shown in Figures 3a and 3b. These spectra show the presence of silicates in the marble. Significant concentrations of Cr, Sb, Zr are noted. The results of the analysis are reported in Tables 1 and 2. These tables show the chemical analysis of two different spots in the marble, where silicate mineral was identified. .

Vibrational Spectroscopy

The Raman spectra over the 100 to 1500 cm^{-1} spectral range of selected crystals embedded in the hard white marble are shown in Figure 4. This figure displays the recorded spectrum together with the Raman spectrum of allanite downloaded from the RRUFF data base. A strong similarity is observed between the two spectra. These spectra may be subdivided into sections depending upon the type of vibration being studied. The Raman spectra of the series of allanite and the RRUFF allanite over the 750 to 1150 cm^{-1} spectral range are reported in Figure 5. Raman bands are observed in this spectrum at 816, 1057 and 1105 cm^{-1}. These bands are attributed to SiO stretching vibrations. The RRUFF Raman spectrum suffers from a lack of signal. Bands in the RRUFF spectrum are observed at 806 and 1053 cm^{-1}. There is good agreement in this spectral region.

The Raman spectra of allanite and the RRUFF allanite over the 350 to 750 cm^{-1} spectral range are reported in Figure 6. Raman bands are found in the allanite from the Chillagoe marble at 409, 439, 493, 603, 609, 631, 656 and 692 cm^{-1}. Raman bands in the RRUFF Raman spectrum are observed at 409, 495, 603 and 657 cm^{-1}. These bands are attributed to siloxane bending modes. The Raman spectra of the series of allanite and the RRUFF allanite over the 100 to 350 cm^{-1} spectral range are reported in Figure 7. Two Raman peaks are observed in the RRUFF spectrum at 225 and 289 cm^{-1}. In the Raman spectrum of allanite located in the marble, bands are found at 153, 225, 244,271, 280, 294 and 304 cm^{-1}. These bands are simply described as lattice vibrations. It is not expected that the spectra of the marble allanite and that from the RRUFF data base would be identical. This is quite common for two minerals from different origins.

The Raman spectrum of allanite over the 1150 to 1550 cm^{-1} spectral range is reported in Figure 8. An intense Raman band is observed at 1316 cm^{-1} with shoulder bands at 1271, 1351 and 1403 cm^{-1}. This band may be assigned to an antisymmetric stretching vibration.

Conclusions

Specimens of marble from Chillagoe contain many different crystals including calcite and aragonite as well the mineral allanite. Crystals in the marble were analysed using SEM with EDS and the chemistry of selected silicate mineral crystals was determined. The Raman spectra of these crystals were obtained. In order to ascertain the identity of the crystals, we turned to the RRUFF data base based upon the SEM/EDS analyses and identified the silicate mineral which had a similar spectrum to our crystals in the Chillagoe marble as allanite. The Raman spectrum of allanite from this work corresponds excellently well with the Raman spectrum of allanite from the RRUFF data base.

Acknowledgements

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162
163
164

List of Figures

List of Tables

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard
O	K series	24.48	0.08238	50.41	0.46	SiO2	Yes
Na	K series	1.00	0.00422	1.34	0.10	Albite	Yes
Mg	K series	0.20	0.00130	0.28	0.06	MgO	Yes
Si	K series	0.24	0.00187	0.25	0.05	SiO2	Yes
S	K series	0.49	0.00418	0.45	0.05	FeS2	Yes
Zr	K series	4.53	0.03955	4.15	0.08	NaCl	Yes
K	K series	32.80	0.27786	28.71	0.30	KBr	Yes
Ca	K series	7.98	0.07130	8.25	0.16	Wollastonite	Yes
Cr	L series	4.19	0.03771	4.26	0.44	InAs	Yes
Sb	L series	1.66	0.01663	1.91	0.34	Sb	Yes
Total:				100.00			

Table 1 Chemical analysis of a crystal using EDS of a silica containing mineral

206

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard
O	K series	65.64	0.22089	47.66	0.22	SiO2	Yes
Mg	K series	15.33	0.10166	14.40	0.12	MgO	Yes
Al	K series	10.73	0.07705	11.09	0.11	Al2O3	Yes
Si	K series	16.21	0.12844	16.79	0.13	SiO2	Yes
Zr	K series	0.17	0.00151	0.16	0.04	NaCl	Yes
K	K series	0.50	0.00422	0.38	0.04	KBr	Yes
Ca	K series	4.08	0.03641	3.13	0.06	Wollastonite	Yes
Fe	K series	6.45	0.06445	5.72	0.12	Fe	Yes
Cr	K series	0.72	0.00723	0.67	0.12	Zn	Yes
Total:				100.00			

207

208 **Table 2 Chemical analysis of a second crystal using EDS of a silica containing mineral**

209

Figure 1

Figure 2a

Figure 2b

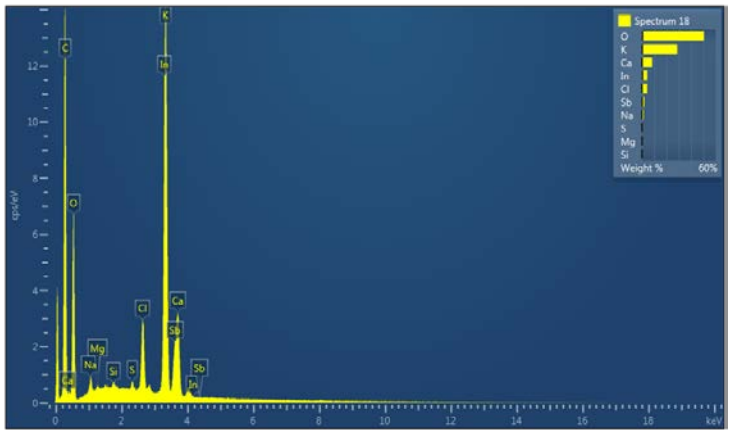

Figure 3a

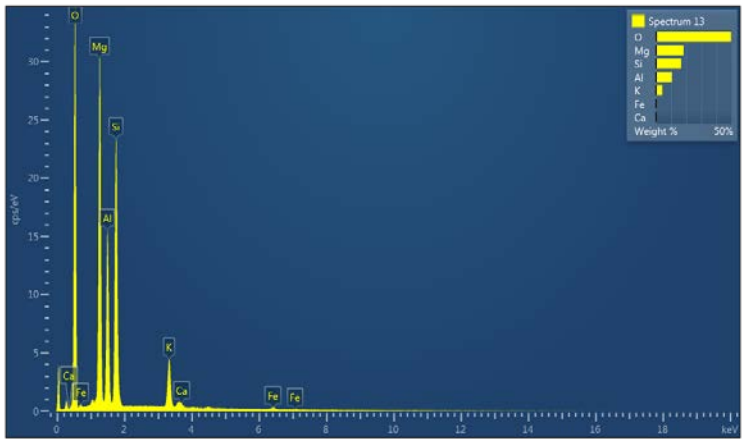

Figure 3b

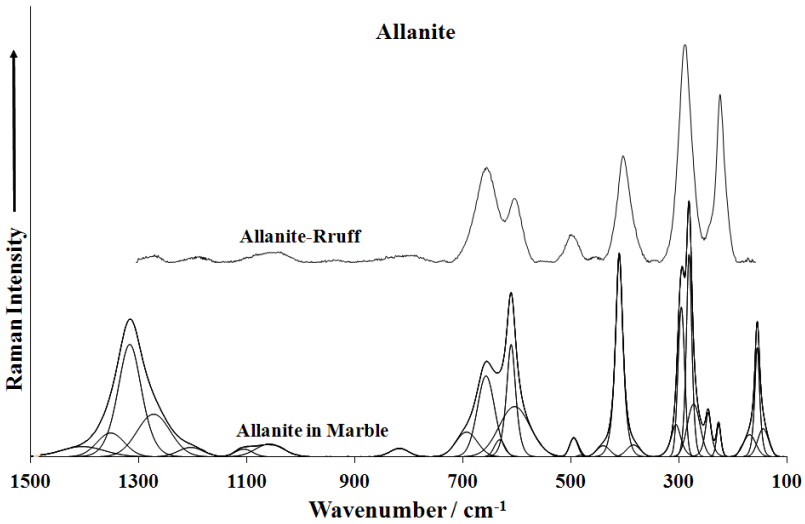
Allanite
Allanite-Rruff
Allanite in Marble
Raman Intensity
1500
1300
1100
900
700
500
300
100
Wavenumber / cm-1

Figure 4

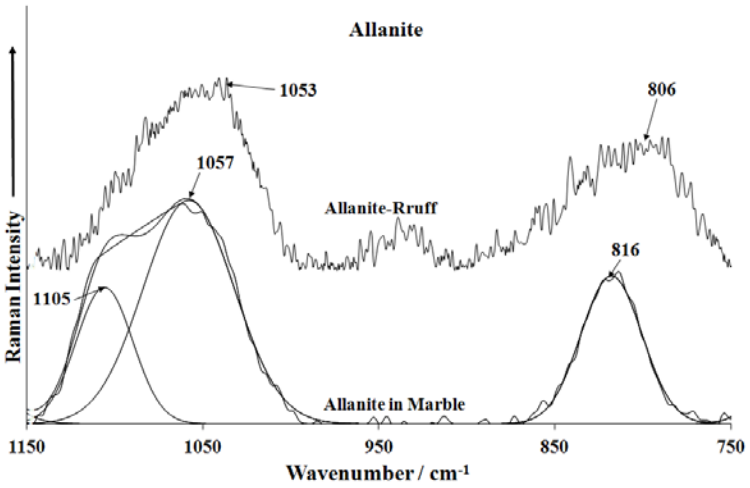
Allanite
1053
806
1057
Allanite-Rruff
816
1105
Allanite in Marble
Raman Intensity
1150
1050
950
850
750
Wavenumber / cm-1

Figure 5

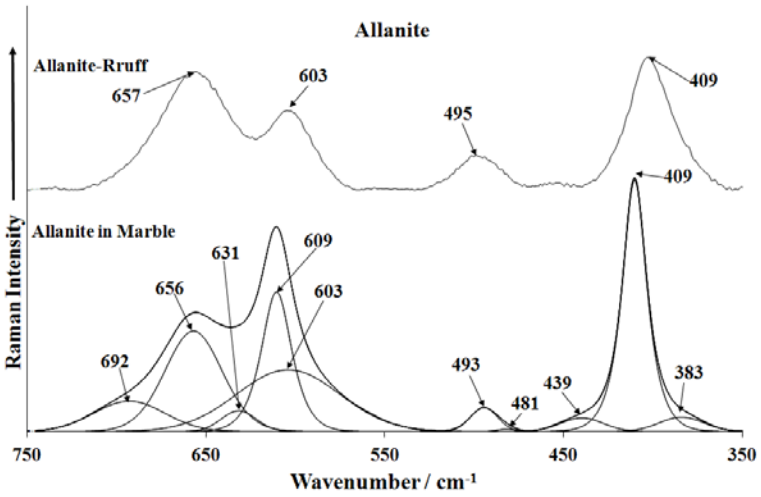
Allanite
Allanite-Rruff
657
603
495
409
409
Allanite in Marble
631
609
656
603
692
493
439
481
383
Raman Intensity
750
650
550
450
350
Wavenumber / cm-1

Figure 6

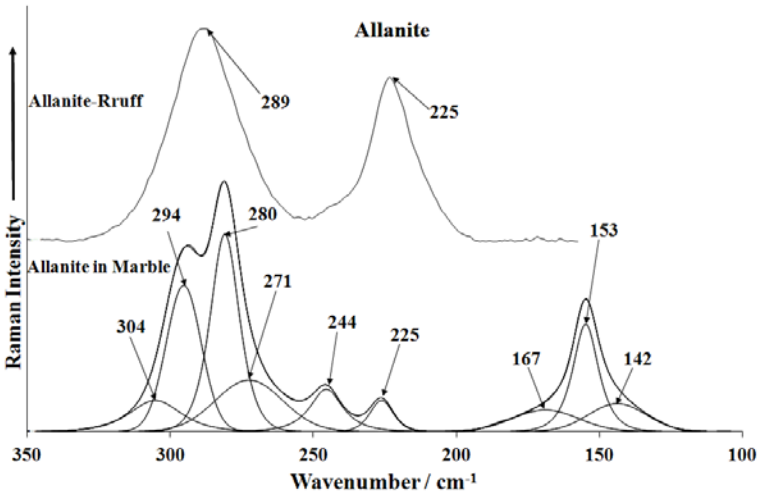
Allanite
Allanite-Rruff
289
225
294
280
153
Allanite in Marble
271
304
244
225
167
142
Raman Intensity
350
300
250
200
150
100
Wavenumber / cm-1

Figure 7

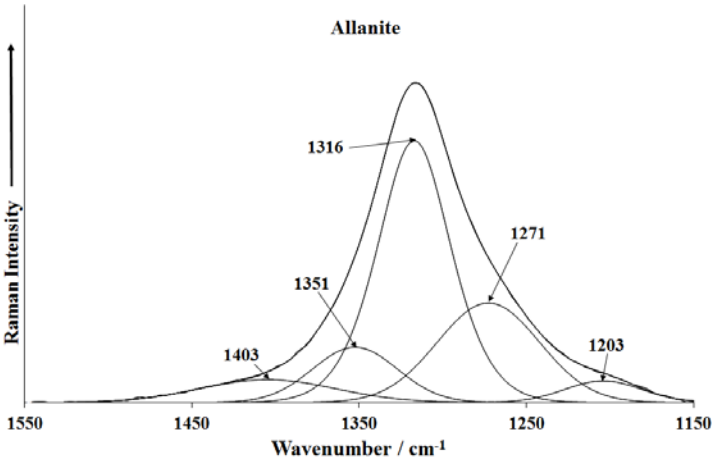
Allanite
1316
1271
1351
1403
1203
Raman Intensity
1550
1450
1350
1250
1150
Wavenumber / cm-1

Figure 8